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FACTORS AFFECTING THE REMOVAL OF RADIOSTRONTIUM FROM MILK BY ION EXCHANGE RESINS

SUMMARY

The effect of temperature, flow rate, and direction of flow through columns of cationic ion exchange resins on the removal of radiostrontium from milk was studied. The milk was in vivo labeled with Sr^{85}. Milk temperature within the range of 40 to 80 F did not affect the amount removed (about 85%) when the milk was acidified to a pH of 5.4. When milk was passed through at normal pH (6.65), about 8% more removal was obtained at 100 F than at 40 F. No further increase was obtained by heating the milk to 180 F. However, less than half of the strontium was removed from nonacidified milk regardless of temperature. The temperature studies were carried out at a flow rate of 0.5 resin bed volume (rbv) per minute.

The amount removed from the first 30 rbv decreased from 96 to 71% as the flow rate was increased from 0.125 to 2.00 rbv per minute.

Studies comparing the relative effectiveness of downflow and upflow of milk through the columns showed that about 8% more strontium was removed by downflow at a flow rate of 0.25 rbv per minute and 12% more at 1.0 rbv per minute.

Several ion exchange resin techniques for removing radiostrontium from milk have been suggested. Because of the limited data available in the literature, the development of a practical removal method requires a study of several factors which affect the efficiency of the procedure.

Various resin forms and methods of treating milk with the resins have been reported. Nervick et al. (8), and Easterly et al. (3), used resins in the sodium form to remove most of the radiostrontium from milk. Gluekauf et al. (5) and Cosslett and Watts (2) describe removal of radiostrontium by passing the milk through a cation exchange resin in the calcium form. Single-ion resin forms result in drastic changes in the cationic composition of milk. Migicovsky (6) used a mixed form (Ca K Na) to minimize these changes. Murthy et al. (7) showed that a marked increase in the removal of radiostrontium is obtained by acidifying milk to a pH of 5.2-5.4 with citric acid before passing through columns of ion exchange resin. The resin was used in a Ca, Mg, K, Na form. They reported that the removal of radionuclides did not vary with flow rates of 5-25 ml per minute per 30 g of resin in test columns. These results were obtained with milk equilibrated with Sr^{85} for 24 hr.

Migicovsky (6) reported briefly on the effect of temperature on strontium removal from milk in batch systems. Baker and Gehrke (1) reported little change in the exchangeability of calcium in skimmilk heated to temperatures of 40, 60, and 80 degrees centigrade for 30-min periods. Employing the batch method, Easterly et al. (3) showed that the amount of strontium and calcium removed increased with contact time; up to 94% of radiostrontium was removed.

The present experiment was designed to determine the effect of temperature, direction of milk flow, milk flow rate, and quantity of milk passed through an ion exchange column, on the removal of strontium from milk.

EXPERIMENTAL PROCEDURE

A Holstein cow was given an average daily dose of 0.5 mc of $Sr^{85}(NO_3)_2$ for the duration of this experiment. $Strontium^{85}$ was used in these experiments to determine the efficiency of removal of radiostrontium from milk. Since the order of magnitude of this isotope secreted in the milk was many times less than the naturally occurring strontium, the percentage removal of all strontium isotopes, including stable strontium, Sr^{85}, and Sr^{90} will not be influenced by daily variations of Sr^{85} in the milk.

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[1] U. S. Public Health Service, Department of Health, Education and Welfare, Washington, D. C.

[2] A joint research project supported by the AEC and PHS.

Daily milk samples from this cow (composites of AM and PM) were passed through an ion exchange column 1.5 in. in diameter containing 100 ml of IR-120 resin, except as otherwise specified. The resin used was regenerated by passing 25 ml of charging solution per milliliter of resin through a resin column at a flow rate of 0.25 resin bed volumes (rbv) per minute. The charging solution contained 625, 83, 217, and 385 meq of Ca, Mg, Na, and K, respectively. This is approximately ten times the concentration of these ions in normal milk. After thoroughly mixing the resin, 100-ml aliquots were taken from the resin stock as needed for daily use. Before each trial, the resin was rinsed with distilled water until a negative chloride test was observed. The excess water was flushed from the resin, with the first 100 ml of milk passing through the column and discarded. The remainder of the milk passing through the column was collected in 500-ml fractions (five bed volumes per fraction).

(A) *Effect of milk temperature.* For the studies concerned with variable temperatures a constant flow rate of 0.5 ml of milk per milliliter of resin was maintained. Milk was passed through the column continuously until ten fractions (50 bed volumes) were collected. Trials were made at temperatures of 40, 60, and 80 F for milk at a pH of 5.4 and at 40, 60, 80, 100, 140, and 180 F for normal milk. Trials at temperatures in excess of 80 F with milk at pH of 5.4 were not practical, due to frequent coagulation. To insure constant temperature throughout each trial, a water jacket was used around the resin columns. The water was constantly flowing into the jacket and being pumped back into a constant-temperature water bath.

At the beginning of each trial the milk was thoroughly mixed and divided into two equal portions. Both portions were brought to the desired experimental temperature and then one adjusted to a pH of 5.4 by the addition of 0.5 M citric acid, the other portion remaining at the pH of normal milk. The milk portions (pH 5.4 and normal milk) were run at the above-indicated temperatures. Duplicate runs were made for each treatment, and all samples were analyzed in duplicates and the averages reported.

For analysis, 15.0-ml aliquots were taken from each portion of milk, before exposure to the resin, and used as standards, and from each five bed volume fraction of resin-treated milk. The activity was calculated as a per cent of the standard. All milk samples were counted with a Nuclear-Chicago model 132-A automatic single-channel gamma spectrometer.[3] The 0.95 counting error was less than 2%.

In another phase of this experiment, normal milk (pH approx 6.65) was passed through jacketed columns at flow rates of 0.25 and .0625 rbv per minute. The milk was preheated to 145 F and maintained at this temperature (by use of water jackets around the columns) during passage through the exchange column. The sampling, counting, and other experimental conditions were the same as described above.

(B) *Effect of flow rate through columns.* Since the milk-resin contact time has been shown to be an important factor in the removal of strontium (and calcium) from milk by the batch method (4), this variable was studied by use of ion exchange columns and expressed as flow rate. The experiment was designed as a five by two by ten factorial. The variables included were five flow rates, two pH values, and ten successive effluent milk samples. Each treatment had two replicates. Flow rates of 0.125, 0.25, 0.50, 1.00, and 2.00 ml of milk per milliliter of resin per minute were used. The pH levels were 5.4 and 6.65. Fifty bed volumes of milk were passed through an ion exchange column 2 cm in diameter, containing 50 ml of resin. All trials were made at room temperature (75 F). The same type milk, resin, charging solution, sampling and counting procedures were used as described for the temperature studies.

(C) *Effect of direction of flow through the columns.* To determine the effect of milk flow direction through the columns, 15 bed volumes of milk were passed through each of six ion exchange columns. Three of the columns were operated downflow at rates of 0.25, 0.50, and 1.00 rbv per minute, whereas the three others were operated upflow at the same rates. The columns and milk were maintained at room temperature throughout the trials. All other factors were constant and the same procedures used as described previously, with the exception of sampling frequency. Aliquot milk samples were taken from each three bed volume fractions passing through the columns.

RESULTS AND DISCUSSION

The effect of temperature on the percentage removal of strontium from milk at a pH of 5.4 and 6.65 (normal milk) is shown in Figure 1. Each point represents the mean of the 50 bed volumes passing through the columns at various temperatures. It will be noted that the per-

[3] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

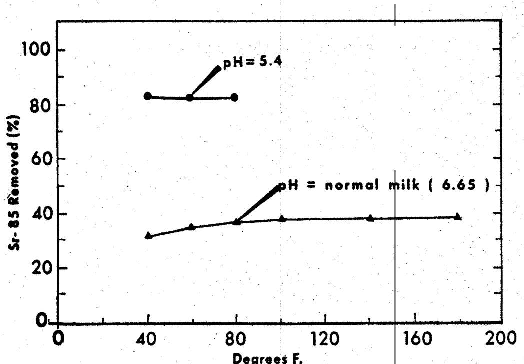

FIG. 1. Effect of temperature on the removal of Sr^{85} from milk by ion exchange resin.

centage strontium removal is much greater at a pH of 5.4 than at the normal pH of milk. Murthy et al. (7) showed that a marked increase in the amount of strontium removed was obtained by lowering the pH of the milk with citric acid. This is explained by the dissociation of the strontium proteinate complex at lower pH values.

Statistical analysis shows that the effect of temperature on strontium removal was not significant when the pH was maintained at 5.4. However, there was a significant effect from 40 F up to 100 F when normal milk (pH 6.65) was passed through. The small increase in removal may have been due to a slight decrease in pH as the temperature was increased in this range. Milk heated from 40 to 100 F showed a decrease in pH of about 0.20 unit, probably resulting from the dissociation of some of the acid salts. A contributing factor may also be an accelerated exchange rate at higher temperatures.

When combinations of high temperature (145 F) and slow flow rates (0.25 and .0625 resin bed volumes per minute) were used the per cent of strontium removed increased as shown in Table 1.

The effects of flow rate on the removal of strontium at pH 5.4 and 6.65 are shown in Figures 2 and 3, respectively. The percentage removal increased with decreasing flow rates; analysis of variance showed this effect to be highly significant at both pH levels. Again, as in the case of the temperature study, the effect of pH was highly significant.

TABLE 1

Per cent removal of Sr^{85} from milk by exchange resin columns as influenced by a combination of high temperature (145 F) and slow flow rates

5 bed volume portion of elutriated sample	Flow rate .0625	Flow rate 0.25
1	59	52
2	56	51
3	55	51
4	54	49
5	52	48

The removal of strontium, up to 50 bed volumes, at the five flow rates all follow the same general trend, with successive fractions having less removal. However, the slower the flow rate the greater was the volume that could be passed through the columns before an appreciable decrease in the percentage removal was noted at pH 5.4 (Figure 2). The differences in amounts removed at various flow rates increased with increasing volume passed through the columns. This is attributed to greater leakage at the faster rates. This effect is probably accentuated by a small amount of caseinate-complexed strontium, even at a pH of 5.4, which is more slowly exchanged than the unbound portion.

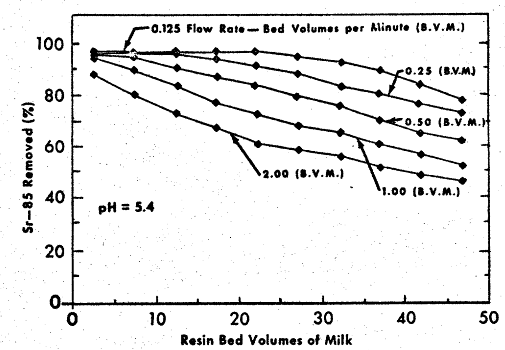

FIG. 2. Effect of flow rate on per cent removal of Sr^{85} from milk by exchange resin columns.

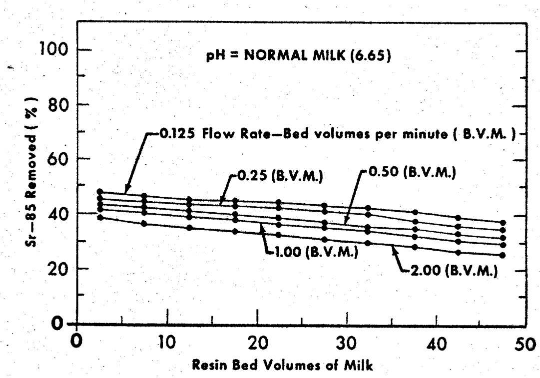

FIG. 3. Effect of flow rate on per cent removal of Sr^{85} from milk by exchange resin columns.

At pH 5.4 the average removal for the first 30 bed volumes of milk at flow rates of 0.125 and 1.0 resin bed volumes per minute was 96.7 and 81.1%, respectively. Murthy et al. (7)

reported no variation in the per cent of Sr^{85} removed under similar conditions within a fivefold flow rate range. However, the volume of milk collected for analysis was not reported. If only a few volumes of effluent were analyzed, the effect of flow rate would be less marked. Also, the studies reported by Murthy et al. (7) were made by using in vitro-labeled milk.

Results from the flow rate studies are in agreement with previous work (4) which showed that milk-resin contact time had a significant effect on the removal of strontium and calcium from milk.

Figure 4 shows the effect of flow direction (up vs. down) on strontium removal from milk. Downflow shows an advantage of approximately 8% at the flow rate of 0.25 and 12% at 1.00. This could be due to the turbulent action of the milk on the resin when the upflow procedure is employed, causing it to act more like a batch procedure. Under these conditions, the chromatographic effect of the column is lost.

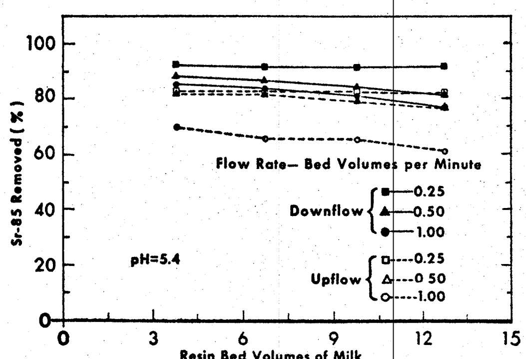

FIG. 4. The effect of direction of flow (downflow vs. upflow) on removal of Sr^{85} from milk.

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